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GJ

(56) Documents cited

GB A 2096134	GB A 2068574
GB A 2092323	GB A 2055803
GB A 2092321	GB A 2052082
GB A 2092320	GB A 2034494
GB A 2091434	GB A 2034493
GB A 2088074	

(58) Field of search
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(54) Electrophotographic photosensitive member

(57) An electrophotographic photosensitive member comprises a charge generation layer and a charge transport layer containing a hydrazone compound. The electrophotographic member is suitable for use in a laser printer. A preferred charge generating compound is amorphous silicon.

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SPECIFICATION

Electrophotographic photosensitive member

5 The present invention relates to electrophotographic photosensitive members and more particularly to electrophotographic photosensitive members containing hydrazone group compounds. 5

Inorganic photoconductive substances such as selenium, cadmium sulfide, and zinc oxide have so far been used over a wide range in photosensitive layers of electrophotographic photosensitive members. The photosensitive members employing such inorganic photoconductors involve various disadvantages along with several advantages. Examples of the disadvantages are as follows: In the case of selenium, the 10 production cost of the photosensitive member is high because of its low productivity, severe conditions of production, and loss of the raw material, which are attributable to the vacuum deposition process, and in addition the deposited film of selenium itself has extremely poor resistance to heat and mechanical shocks and is very liable to crystallize under certain environmental conditions. In the case of a photosensitive 15 member made of cadmium sulfide, the photosensitive member stored under high humidity cannot exhibit stable sensitivity or durability upon using. In the case of a photosensitive member made of zinc oxide, the photosensitive member is subject to charge deterioration and light fading due to corona charging, since the sensitization is effected by use of a dye of poor fastness, typified by Rose Bengal. This type of photosensitive member has also disadvantages in smoothness, hardness, and wear resistance of the photosensitive layer 20 surface thereof because it is a dispersion system of zinc oxide particles in a resin.

In contrast to inorganic photoconductive substances, organic ones have the advantage of giving a highly flexible photosensitive layer and photosensitive members of stable electrophotographic characteristics with ease and low costs, so that in recent years many proposals have been made.

The following types of photosensitive members are known as those employing organic photoconductive 25 substances:

(1) A charge-transfer complex is formed by combining an electron donor with an electron acceptor (e.g. U.S. Patent No. 3,484,237).

(2) An organic photoconductor is sensitized by addition of a dye (e.g. Japanese Patent Publication No. 25,658/1973).

(3) A pigment is dispersed in a positive hole matrix or an electronically active matrix (e.g. U.S. Patent Nos. 30 3,894,868 and 3,870,516).

(4) An electrophotographic photosensitive member comprises a charge generation layer and a charge transport layer (e.g. U.S. Patent No. 3,837,851).

(5) An electrophotographic photosensitive member comprises a co-crystalline complex containing a dye 35 and a resin (e.g. U.S. Patent No. 3,684,502).

(6) An organic pigment or an inorganic charge generation material is added to a charge-transfer complex (e.g. U.S. Patent No. 3,775,105).

(7) Other types.

Present aspects of these types of photosensitive members are that further improvements in sensitivity, 40 durability, environmental stability, etc. are desired though actually useful ones are found among them.

These organic photoconductive substances for such photosensitive members include high-molecular compounds typified by poly(N-vinylcarbazole) and low-molecular compounds such as pyrazoline derivatives disclosed in U.S. Patent No. 3,837,851.

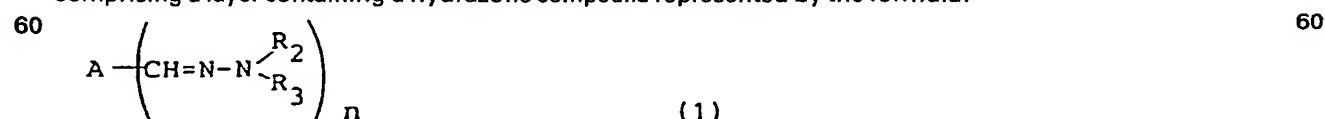
High-molecular photoconductive substances generally give brittle coatings and are deficient in film 45 forming property and in flexibility. Addition of a plasticizer to remove these drawbacks is accompanied by alternative drawbacks such as reduction of sensitivity. On the other hand, low-molecular ones can be freed from such drawbacks as high-molecular ones have, by choosing a proper binder, but cannot be said to be satisfactory in sensitivity, durability, and environmental stability.

Sensitivity of conventional photosensitive members, which is represented in exposure quantity for halving 50 original potential, $E_{1/2}$ is about 15 lux.sec for unsensitized Se type and in the order of 4 - 8 lux.sec for sensitized Se type. Sensitivity of CdS type is similar to that of sensitized Se type, and that of ZnO type about 7 - 12 lux.sec.

As a desirable sensitivity of practical photosensitive member, $E_{1/2}$ value is to be 20 lux.sec or lower in the case of a usual PPC copying machine, more preferably 15 lux.sec or lower in the case of a high-speed PPC 55 copying machine, but a photosensitive member of sensitivity lower than that mentioned above may be used.

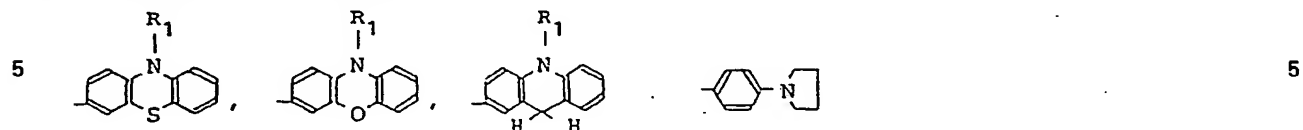
An object of the present invention is to provide an electrophotographic photosensitive member as free as possible of the foregoing disadvantages, and having improved sensitivity.

According to the present invention, there is provided an electrophotographic photosensitive member comprising a layer containing a hydrazone compound represented by the formula:



65 wherein R_2 and R_3 are each unsubstituted alkyl or substituted alkyl, unsubstituted aralkyl or substituted 65

aralkyl, or unsubstituted aryl or substituted aryl with the exception that R_2 and R_3 are alkyls at the same time, n is 1 or 2, when n is 1 A represents

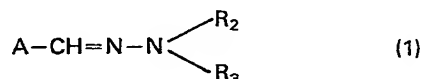


wherein R_1 is C_1 - C_5 alkyl, unsubstituted or substituted aralkyl, and when n is 2 A represents a direct single bond between two

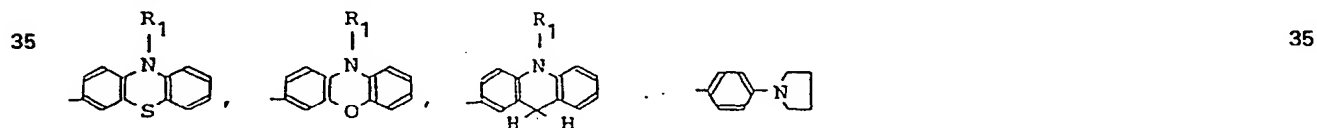


Preferably the electrophotographic photosensitive member, as described above, wherein the electro-photographic photosensitive member comprises a conductive layer, a charge generation layer, and a charge transport layer which contains a said hydrazone compound.

20 The specific hydrazone compounds used in the present invention are represented by the formula: 20



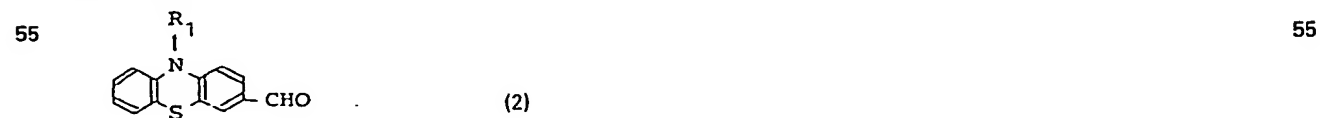
25 In this formula, R_2 and R_3 are each selected from the following radicals: linear or branched C_1 - C_5 alkyls such as methyl, ethyl, propyl, and butyl; aralkyls such as benzyl, phenethyl, and naphthylmethyl; and aryls such as phenyl, naphthyl, anthryl, and pyrenyl. These alkyls, aralkyls, and aryls may also have substituents, which 30 include alkoxy radicals such as methoxy, ethoxy, propoxy, and butoxy; dialkylamino radicals such as dimethylamino, diethylamino, dipropylamino, and dibutylamino; and halogen atoms such as chlorine, bromine, and iodine. The benzene rings or aryl radicals of these aralkyl radicals may also be substituted by alkyl radicals such as methyl, ethyl, propyl, and butyl, n is 1 or 2. When n is 1, A in formula (1) represents

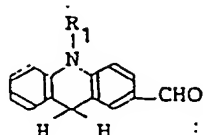


40 wherein R_1 is C_1 - C_5 alkyl (e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-amyl, or t-amyl) or aralkyl (e.g. benzyl, phenethyl or naphthylmethyl), and the benzene rings of the above-mentioned aralkyl may also have the following substituents: alkyls such as methyl, ethyl, propyl, and butyl; alkoxy radicals such as methoxy, ethoxy, propoxy, and butoxy; dialkylamino radicals such as dimethylamino, diethylamino, dipropylamino, and dibutylamino; and halogen atoms such as chlorine, bromine, and iodine. When n is 2, A represents a 45 direct single bond between two

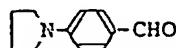


These hydrazone compounds can be prepared in the usual way by reacting aldehyde compounds with hydrazines or with mineral acid salts thereof when n is 1, said aldehyde compounds being represented by the formula:



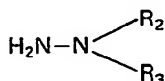


(4)



(5)

10 wherein R_1 is as defined above, and said hydrazines being represented by the formula:



(6)

15 wherein R_2 and R_3 are as defined above. In other words, the hydrazone compounds can be prepared by condensation of aldehyde compounds defined above with hydrazines defined above in a solvent such as alcohol, dimethylformamide, or dimethylsulfoxide and if necessary, in the presence of a small amount of acid (glacial acetic acid or an inorganic acid) as a condensing agent.

20 The hydrazone compounds wherein n is 2 can be prepared in the usual way by reacting glyoxal with hydrazines defined above or with mineral acid salts thereof, that is, by condensation of the above two compounds in a solvent such as alcohol, dimethylformamide, or dimethylsulfoxide and if necessary, in the presence of a small amount of acid (glacial acetic acid or an inorganic acid) as a condensing agent.

25 Specific examples of the hydrazone compounds obtained by the above synthetic method will be illustrated in later examples of carrying out the invention.

Electrophotographic photosensitive members containing a hydrazone compound represented by formula (1) can be applied to any of the foregoing types, (1) - (7), of photosensitive members employing organic photoconductive substances.

30 According to this invention, when a hydrazone compound represented by formula (1) is used as a charge-transport material in the charge transport layer of a photosensitive member of type (4), which has two functionally separated layers, a charge generation layer and a charge transport layer, the sensitivity of the photosensitive member is particularly high and the residual potential thereof is low.

35 In this case, repeated use of the photosensitive member results in less reduction of both the surface potential and the sensitivity and a negligible increase in the residual potential, thus the photosensitive member being excellent in durability. Accordingly, the photosensitive member of type (4) will be explained in more detail below in this invention: The layer construction of conductive layer, charge generation layer, and charge transport layer is essential, and the charge generation layer may be laid either above or below the charge transport layer. For a repeated use type of electrophotographic photosensitive member, however, the lamination in order of conductive layer, charge generation layer, and charge transport layer from bottom to top is preferred mainly in view of mechanical strength and in certain cases in view of chargeability. A bond layer may be placed between the conductive layer and the charge transport layer for improving the adhesion.

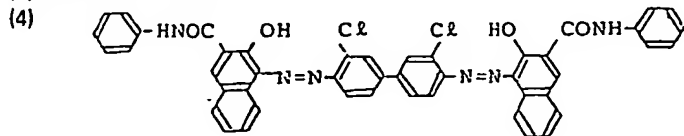
45 The conductive layer to be used includes a plate or foil of metal such as aluminum, plastic film onto which aluminum or another metal has been metalized by vacuum deposition, paper or plastic film each overlaid with aluminum foil, and conductivized paper.

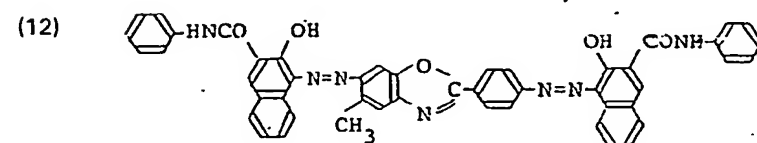
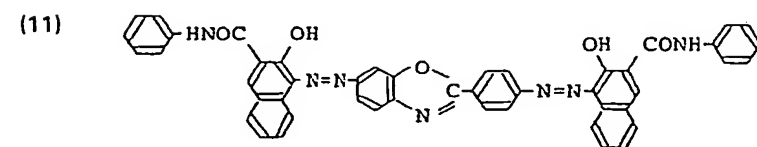
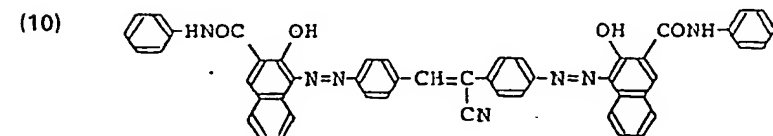
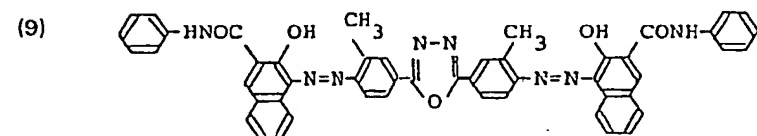
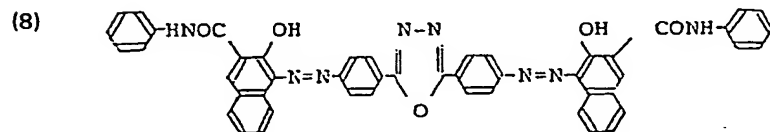
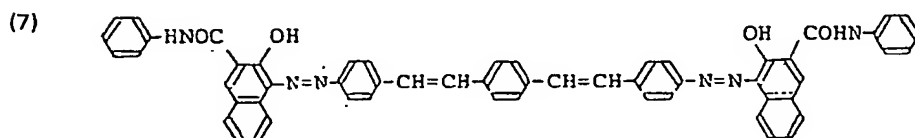
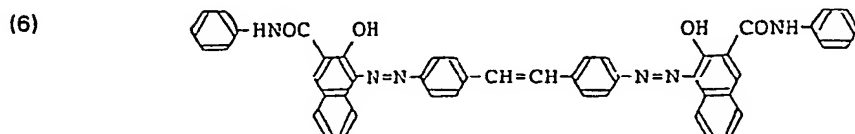
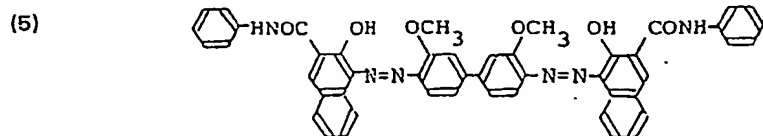
Effective materials for use as the bond layer are casein, poly(vinyl alcohol), water-soluble ethylene-acrylic acid copolymer, and nitrocellulose. Thickness of the bond layer is $0.1 - 5\mu$, preferably $0.5 - 3\mu$.

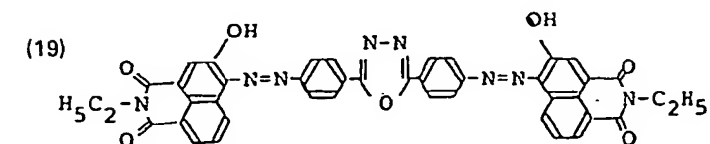
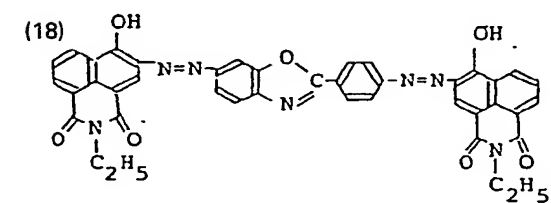
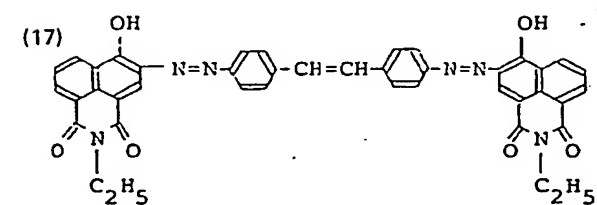
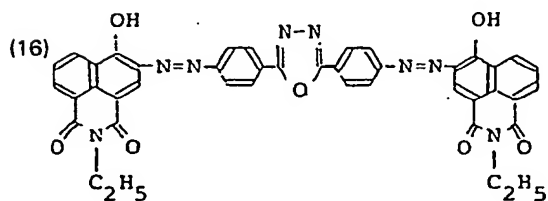
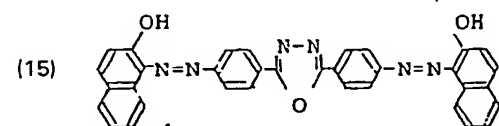
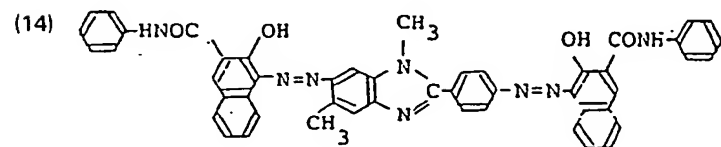
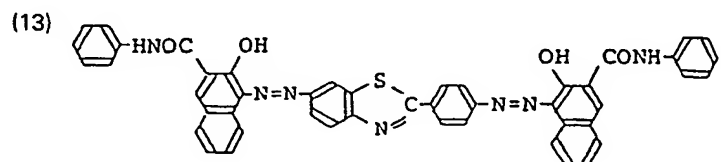
50 The charge generation layer materials are not limited to combinations with particular substances. This layer may be a vacuum-deposited layer, a layer combining a charge generation material with a binder resin, or a resin-free layer comprising a dye or pigment, of which charge generation materials are selected from a variety of materials capable of generating charge carriers at high efficiency, which include inorganic substances such as selenium, selenium-tellurium, selenium-arsenic, cadmium sulfide, and amorphous silicon and organic substances such as pyrylium dyes, thiapyrylium dyes, triarylmethane dyes, thiazine dyes, cyanine dyes, phthalocyanine pigments, perylene pigments, indigo pigments, thioindigo pigments, quinacridone pigments, squaric acid pigments, azo pigments, and polycyclic quinone pigments. Thickness of the charge generation layer is 5μ or less, preferably $0.01 - 1\mu$.

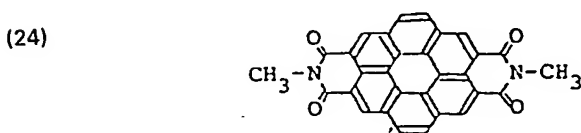
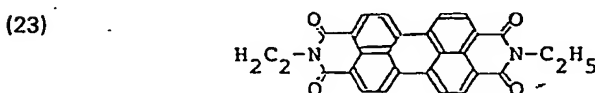
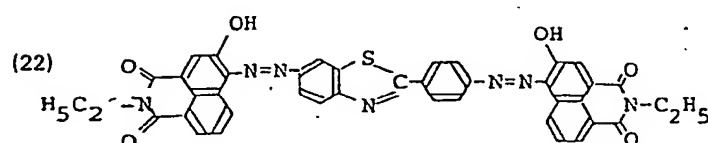
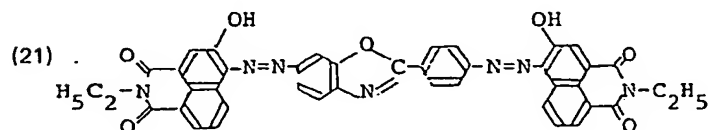
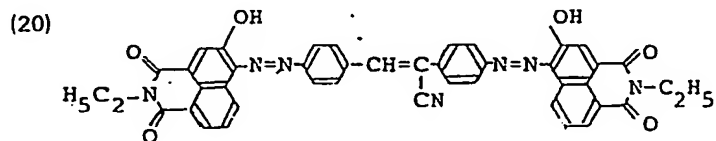
Typical examples of charge generation materials usable in this invention are recited as follows:

- (1) amorphous silicon
- (2) selenium-tellurium
- (3) selenium-arsenic









(25) β -form copper phthalocyanine

When the charge generation layer is formed by coating a dispersion of charge generation material in a resin solution or a solution of charge generation material, a large amount of binder added has an adverse effect on the sensitivity of the layer, so that the binder content in the charge generation layer is desirably up to 80% by weight, still preferably up to 40% by weight. Many kinds of resin can be used as the binder for the charge generation layer, such as poly(vinyl butyral), poly(vinyl acetate), polyesters, polycarbonates, phenoxy resins, acrylic resins, polyacrylamide, polyamides, poly(vinylpyridine), cellulosic resins, urethane resins, epoxy resins, casein, and poly(vinyl alcohol).

The charge generation layer thus formed is overlaid with the charge transport layer of 5 - 30 μ , preferably 8 - 20 μ , in thickness.

The hydrazone compounds of this invention do not have film-forming ability in themselves, so that the charge transport layer is formed by coating and drying in the usual way of a solution prepared by dissolving each of the hydrazone compounds together with one of the following various binder resins in a suitable solvent. The binder resins for the charge transport layer include acrylics, polystyrenes, polyesters, phenoxy resins, polycarbonates, silicone resins, epoxy resins, urethane resins, and also hole-transporting polymers such as poly(N-vinylcarbazole).

The hydrazone compounds of this invention are hole-transporting materials. Accordingly, when operating a photosensitive member prepared by the lamination in order of conductive layer, charge generation layer, and charge transport layer, it is necessary to negatively charge the surface of charge transport layer. In the exposed areas, upon exposure after charging, holes produced in the charge generation layer are injected into the charge transport layer, then arrive at the surface, and neutralize negative charges to attenuate the surface potential, thus resulting in electrostatic contrasts between exposed and unexposed areas. The latent electrostatic image thus produced is developed with a positively chargeable toner to form a visible image. This visible image can be fixed either directly or after transferred to paper, plastic film, or the like. The latent electrostatic image on the photosensitive member can also be transferred onto the insulating layer of a transfer paper and then developed and fixed. The type of developer, the developing method, or the fixing method in these operations is not limited to specific ones: any of known developers and known developing or fixing methods may be adopted.

Photosensitive members of other types than type (4) are now briefly explained though they are described in detail in the references cited above.

Since a charge transfer complex is formed by combining an electron attractive substance with a hydrazone compound of this invention, a photosensor of type (1) can be obtained by coating a solution of the charge transfer complex and a binder resin in a suitable solvent on a conductive layer or on a bond coating thereof and drying it, in the usual way.

5 The electron attractive substances usable in this case include low-molecular substances such as chloranil, bromanil, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitrofluorenone, 2,4,7-trinitro-9-dicyanomethylene fluorenone, 2,4,5,7-tetranitroxanthone, and 2,4,8-trinitrothioxanthone; and such polymers of electron attractive substances as described in U.S. Patent No. 4,122,113. Various kinds of binder stated referring to the photosensitive member of type (4) can be used for
10 this type of photosensitive member.

A photosensitive member of type (2) can be obtained by dissolving a hydrazone compound of this invention and a binder for the charge transport layer of the photosensitive member of type (4) mentioned above in a suitable solvent, further adding one of the various kinds of dye or pigment stated referring to the photosensitive member of type (4), coating this solution on a conductive layer or on a bond layer thereupon,
15 and drying it, in the usual way.

A photosensitive member of type (3) can be obtained by adding one of the various kinds of dye or pigment stated referring to the photosensitive member of type (4), to a hydrazone compound of this invention, which serves as a hole matrix.

A photosensitive member of type (5) can be prepared from three components, i.e., a pyrylium dye such as
20 2,6-diphenyl-4-(N,N-dimethylaminophenyl)thiapyrylium perchlorate, a resin, for example, polycarbonate, capable of forming a co-crystalline complex with said dye, and a hydrazone compound of this invention.

A photosensitive member of type (6) can be prepared by adding one of the various kinds of charge generation materials stated in reference to the photosensitive member of type (4), to a charge-transfer complex analogous to those for use in the photosensitive member of type (1).

25 The electrophotographic photosensitive members of this invention can be utilized not only in electrophotographic copying machines but also in a wide range of electrophotographic applications such as laser printers, CRT printers, and electrophotographic printing plate making systems.

An example of process for synthesizing the hydrazone compound of this invention will be described below.

30 *Synthetic process example*

Synthesis of N-ethylphenothiazine-3-aldehyde-N',N'-diphenylhydrazone

To 50 ml of ethanol were added 5.77g (0.0226 mol) of N-ethylphenothiazine-3-aldehyde, 5.0g (0.0226 mol) of N,N-diphenylhydrazine hydrochloride, and 2 ml of acetic acid, and the mixture was stirred at room
35 temperature for 1 hour. The resulting liquid was filtered, and the solid fraction was dispersed in a dilute aqueous ammonia, filtered, washed and then dried. The solid matter obtained was recrystallized from methyl ethyl ketone, giving 3.0g of yellow crystals, m.p. 137.2 - 138.5°C, yield 32%.

Elemental analysis (%):

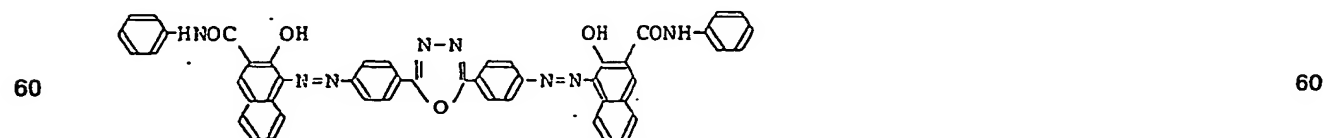
40	Calcd. for $C_{27}H_{23}N_3S$	Found	40
	C	76.92	
	H	5.51	
45	N	9.97	45

I.R. absorption spectrum:

The absorption at 1670cm^{-1} (C=O stretching band) observed for the starting aldehyde was disappeared.
50 Other hydrazone compounds for use in this invention can be synthesized in a similar way.
For illustrating the invention in more detail, the following examples are given.

Example 1

A solution of casein in aqueous ammonia (11.2g of casein, 1g of 28% aqueous ammonia in 222 ml of water)
55 was coated by means of a Meyer bar on an aluminum plate and dried to form a bond layer of 1.0 g/m^2 .
Then, 5g of a pigment of the formula



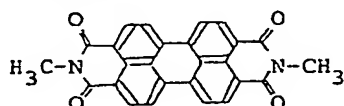
was dispersed in a solution of 2g of vinyl butyral resin (butyral conversion degree 63 mol%) in 95 ml of ethanol by using a ball mill. The dispersion thus obtained was coated on the bond layer by means of a Meyer
65 bar to form a charge generation layer of 0.2 g/m^2 . Subsequently, a solution of both 5g of N-

ethylphenothiazine-3-aldehyde-N',N'-diphenylhydrazone and 5g of polycarbonate of 2,2-bis(4-hydroxyphenyl) propane (mol. wt. 30,000) in 70 ml of tetrahydrofuran was coated on the charge generation layer and dried to form a charge transport layer of 10 g/m².

The electrophotographic photosensitive member thus prepared was conditioned at 20°C under 65% relative humidity, then negatively charged in the static fashion by corona charging at $\ominus 5$ KV using an electrostatic copying paper test device Model SP-428 (supplied by Kawaguchi Denki Co., Ltd.), retained in the dark for 10 seconds, and then exposed to light at 5 lux to examine the charge bearing characteristics. The results showed that Vo was $\ominus 510$ V, Vk 89% and E 1/2 5.7 lux.sec. wherein Vo (–V) is initial potential, Vk(%) potential retentivity after standing in a dark place for 10 seconds, and E 1/2 (lux.sec) exposure quantity for halving initial potential.

Example 2

A pigment of the formula



was vacuum-deposited on the bond surface of the same aluminum plate, having the bond layer, as prepared in Example 1, thereby forming a charge generation layer of 0.15 μ in thickness. The same charge transport layer as in Example 1 was formed on the charge generation layer to prepare a photosensitive member. The results of the same measurements as in Example 1 were as follows:

Vo $\ominus 540$ V, Vk 89%, E 1/2 6.3 lux.sec

Examples 3 - 6

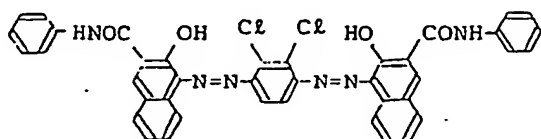
A charge generation layer of selenium-tellurium (tellurium content 10% by weight) of 0.8 μ in thickness was formed by vacuum deposition on an aluminum plate of 100 μ in thickness. A solution of both 5g of a polyester (Vylon 200, made by Toyobo Co., Ltd.) and 5g of each hydrazone compound shown in Table 1 in 70 ml of dichloromethane was coated on the charge generation layer and dried to form a charge transport layer of 10 g/m². The charge bearing characteristics of the photosensitive members prepared in this way were measured in the same manner as Example 1. The results are given in Table 1.

TABLE 1

Example	Hydrazone compound of formula (1)	Vo (–V)	Vk (%)	E 1/2 (lux.sec)
3		540	88	5.4
4		550	89	7.4
5		530	90	7.2
6		560	87	5.8

Example 7

To a solution prepared by dissolving 5g of N-ethylphenothiazine-3-aldehyde-N',N'-diphenylhydrazone and 5g of poly(N-vinylcarbazole) (mol. wt. about 3×10^5) in 70 ml of tetrahydrofuran was added 1.0g of a pigment of the formula

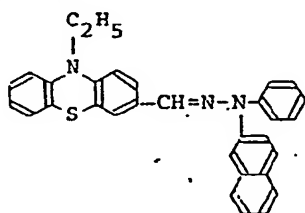


and dispersed by means of a ball mill. The dispersion was coated on the bond surface of the same aluminum plate, having the bond layer, as prepared in Example 1 and dried to form a photosensitive layer of 10 g/m². The charge bearing characteristics of the photosensitive member thus prepared were measured in the same manner as Example 1, except that the charging was positive. The results were as follows:

Vo ⊕500V, Vk 88%, E 1/2 15 lux.sec

Example 8

An aluminum substrate of 0.2mm in thickness was fixed in a vacuum device, which was then thoroughly evacuated, and a gas mixture of hydrogen and silane (15 vol% based on hydrogen) was introduced. Then, a charge generation layer of 0.3μ in thickness of amorphous silicon was formed on the substrate by glow discharge applying a 13.5 MHz high-frequency electric field. After atmospheric pressure was brought back in the vacuum device, the sample plate was taken out and a solution of both 5g of a hydrazone compound of the formula



and 5g of a polyester (Vylon 200, made by Toyobo Co., Ltd.) in 150 ml of dichloromethane was coated on the above-mentioned charge generation layer and dried to form a charge transport layer of 11 g/m². The photosensitive member thus obtained was placed in a charging-exposing test device, corona-charged at ⊖5KV, and subsequently exposed to a pattern of light, which was projected from a tungsten light source through a transmission type test chart. A good toner image was obtained on the surface of the photosensitive member by cascading a positively chargeable developer (containing toner and carrier) thereupon immediately after the exposure.

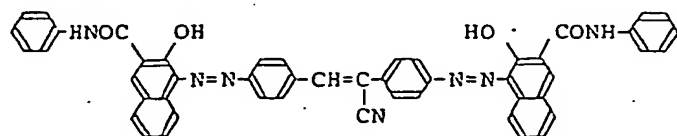
Example 9

A charge generation layer and a charge transport layer were successively laminated on an aluminum plate 0.2mm thick in the same manner as Example 8. Using the photosensitive member thus obtained, a good toner image was obtained in the same procedure as Example 8, except that the corona charging was effected at ⊕5KV and the developer used was of a negatively chargeable type.

Example 10

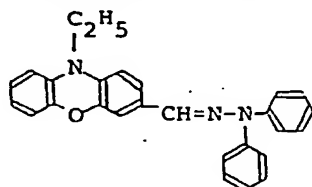
A bond layer of 1.0 g/m² was formed on an aluminum plate by coating an aqueous ammonia solution of casein (11.2g of casein, 1g of 28% aqueous ammonia in 222 ml of water) by means of a Meyer bar and drying it.

Subsequently, a dispersion of 5g of a disazo pigment of the formula



in a solution of 2g of vinyl butyral resin (butyral conversion degree 63 mol%) in 95 ml of ethanol was coated on the bond layer and dried to form a charge generation layer of 0.2 g/m².

Then, a solution of both 5g of a hydrazone compound of the formula



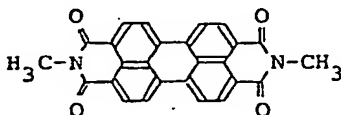
(designated as compound No. H-1) and 5g of polycarbonate of 2,2-bis(4-hydroxyphenyl)propane (mol. wt. about 30,000) in 150 ml of dichloromethane was coated on the charge generation layer and dried to form a charge transport layer of 10 g/m².

The photosensitive member thus prepared was charged at $\ominus 5\text{KV}$ in the static process using the electrostatic copying paper test device Model SP-428 mentioned in Example 1, retained in a dark place for 10 seconds, and exposed to light at 5 lux to examine the charge bearing characteristics. The results were as follows:

$V_o \ominus 530\text{V}$, $V_k 90\%$, $E 1/2 7.0 \text{ lux}\cdot\text{sec}$

Examples 11-20

A charge generation layer of 0.15 μ in thickness was formed on an aluminum plate by vacuum deposition of a pigment of the formula



Then, a solution of both 5g of a polyester resin (Vylon 200, made by Toyobo Co., Ltd.) and 5g of each of hydrazone compound, shown in Table 2, in 150 ml of dichloromethane was coated on the charge generation layer and dried to form a charge transport layer of 11 g/m².

The charge bearing characteristics of the photosensitive member prepared in this way were examined in the same procedure as Example 10. The results are given in Table 3.

TABLE 2

35	Example		Hydrazone compound			35
40		Compound	R ₁	R ₂	R ₃	40
	11	H-2	-C ₂ H ₅		-CH ₃	
45	12	H-3	-C ₂ H ₅		-CH ₂ -	45
	13	H-4	-C ₂ H ₅			
50	14	H-5	-(CH ₂) ₃ CH ₃			50
	15	H-6	-CH ₂ -			
55	16	H-7	-CH ₂ -		-CH ₃	55
	17	H-8	-CH ₂ -			
	18	H-9	-CH ₂ CH ₂ -			
60	19	H-10	-CH ₂ -			60
	20	H-11	-CH ₂ -		-CH ₃	
65						65

TABLE 3

	Example	Compound	Vo (\ominus V)	Vk (%)	E 1/2 (lux.sec)	
5	11	H-2	540	90	11.2	5
	12	H-3	550	91	8.0	
	13	H-4	540	88	7.2	
	14	H-5	560	90	8.0	
10	15	H-6	560	91	7.5	10
	16	H-7	540	93	10.5	
	17	H-8	530	89	7.8	
	18	H-9	560	94	7.5	
	19	H-10	550	90	7.8	
15	20	H-11	560	89	10.8	15

Example 21

A dispersion was prepared by adding 1.0g of β -form copper phthalocyanine to a solution of both 5g of the same hydrazone compound (Compound No. H-2) as used in Example 11 and 5g of poly(N-vinylcarbazole) (mol. wt. about 3×10^5) in 150 ml of dichloromethane. The dispersion was coated by means of a Meyer bar on the casein layer of the same aluminum plate coated with casein as used in Example 10, and dried to form a photosensitive layer of 12 g/m².

The charge bearing characteristics of the photosensitive member thus prepared were measured in the same procedure as Example 10, except that the charging was positive. The results were as follows:

Vo \oplus 510V, Vk 86%, E 1/2 26 lux.sec

Example 22

A charge generation layer of selenium-tellurium (tellurium 10% by weight) 0.8 μ thick was formed on an aluminum plate by vacuum deposition.

Then, a charge transport layer was formed in the same way as Example 13. The charge bearing characteristics of the photosensitive member thus obtained were measured in the same procedure as Example 10. The results were as follows:

Vo \ominus 540V, Vk 90%, E 1/2 6.3 lux.sec

Example 23

An aluminum substrate 0.2mm thick was fixed in a vacuum device and after thorough evacuation of the device, a gas mixture of hydrogen and silane (15 vol% based on hydrogen) was introduced. A charge generation layer of amorphous silicon 0.3 μ thick was formed on the substrate by glow discharge applying a 13.5 MHz high-frequency electric field.

After atmospheric pressure was brought back in the vacuum device, the sample plate was taken out, and a charge transport layer was formed on the charge generation layer in the same way as Example 10.

The photosensitive member thus obtained was placed in a charging-exposing test device, subjected to corona charging at \ominus 5KV, and subsequently exposed to a pattern of light, which was projected from a tungsten light source through a transmission type test chart. A good toner image was obtained on the photosensitive member by cascading a positively chargeable developer (containing toner and carrier) thereupon immediately after the exposure.

Example 24

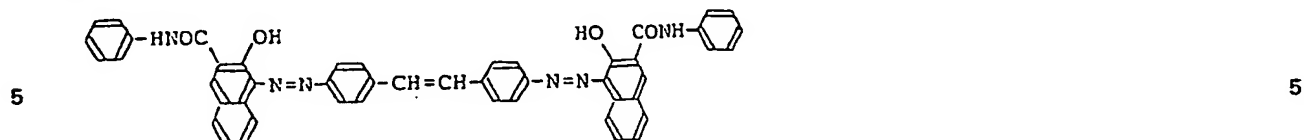
A charge generation layer and a charge transport layer were successively laminated on an aluminum plate 0.2mm thick in the same way as Example 23.

Using the photosensitive member thus obtained, a good toner image was obtained in the same way as Example 23, except that the corona charging was effected at \oplus 5KV and a negatively chargeable developer was used.

Examples 25-33

An aqueous ammonia solution of casein (11.2g of casein, 1g of 28% aqueous ammonia in 222 ml of water) was coated on an aluminum plate and dried to form a bond layer of 1.0 g/m².

Then, a dispersion of 5g of a disazo pigment of the formula:



in a solution of 2g of vinyl butyral resin (butral conversion degree 63 mol%) in 95 ml of ethanol was coated on the bond layer and dried to form a charge generation layer of 0.2 g/m².

10 A solution of both 5g of each hydrazone compound shown in Table 4 and 5g of polycarbonate of 2,2-bis(4-hydroxyphenyl) propane (mol. wt. about 30,000) in 150 ml of dichloromethane was coated on the charge generation layer and dried to form a charge transport layer of 10 g/m².

The photosensitive member thus prepared was subjected to corona charging in the static process at $\ominus 5KV$ using the electrostatic copying paper test device Model SP-428 mentioned in Example 1, retained in a dark place for 10 seconds, and then exposed to light at 5 lux to examine the charge bearing characteristics. The results are shown in Table 5.

TABLE 4

20	Hydrazone compounds					20
25	Example	Compound No.	Hydrazone compound			25
			R ₁	R ₂	R ₃	
30	25	H-12	-C ₂ H ₅			30
	26	H-13	-C ₂ H ₅		-CH ₃	
	27	H-14	-C ₂ H ₅		-CH ₂ -	
35	28	H-15	-C ₂ H ₅			35
40	29	H-16	-(CH ₂) ₃ CH ₃			40
	30	H-17	-CH ₂ -			
	31	H-18	-CH ₂ CH ₂ -		-CH ₃	
45	32	H-19	-(CH ₂) ₂ CH ₃			45
	33	H-20	-CH ₂ -		-CH ₃	

TABLE 5

Charge bearing characteristics

5	Examples	Compound No.	Vo (-V)	Vk (%)	E 1/2 (lux.sec)	5
	25	H-12	500	89	10	
	26	H-13	530	91	15	
10	27	H-14	510	90	13	10
	28	H-15	500	89	11	
	29	H-16	540	94	12	
	30	H-17	490	88	13	
	31	H-18	480	87	16	
15	32	H-19	510	91	12	15
	33	H-20	480	89	15	

Example 34

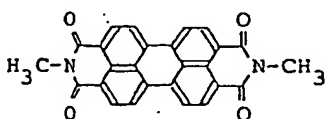
20 A charge generation layer of selenium-tellurium (tellurium 10% by weight) 0.8 μ thick was formed on an aluminum plate by vacuum deposition. 20

Then, a charge transport layer was formed in the same manner as Example 25 to prepare a photosensitive member. The results of measurements of charge bearing characteristics carried out in the same way as Example 25 were as follows:

25 Vo \ominus 520V, Vk 93%, E 1/2 9.0 lux.sec 25

Example 35

30 A charge generation layer 0.15 μ thick of a pigment having the formula 30



35 was formed on an aluminum plate by vacuum deposition. 35

Then, a solution of both 5g of a polyester (Vylon 200, made by Toyobo Co., Ltd.) and 5g of the same hydrazone compound (No. H-15) as used in Example 28 in 150 ml of dichloromethane was coated on the charge generation layer and dried to form a charge transport layer of 11 g/m². The charge bearing characteristics of the photosensitive member thus prepared were measured in the same way as Example 25. The results were as follows:

40 Vo \ominus 520V, Vk 91%, E 1/2 12 lux.sec 40

45 *Example 36* 45

An aluminum substrate 0.2mm thick was fixed in a vacuum device, which was then thoroughly evacuated, and a gas mixture of hydrogen and silane (15 vol% based on hydrogen) was introduced. Then, a charge generation layer 0.3 μ thick of amorphous silicon was formed on the substrate by glow discharge applying a 13.5 MHz high-frequency electric field.

50 After atmospheric pressure was brought back in the vacuum device, the sample plate was taken out, and a charge transport layer was formed on the charge generation layer in the same way as Example 25. The photosensitive member thus obtained was placed in a charging-exposing test device, corona-charged at \ominus 5KV, and subsequently exposed to a pattern of light, which was projected from a tungsten light source through a transmission type test chart. A good toner image was obtained on the surface of the photosensitive member by cascading a positively chargeable developer (containing toner and carrier) thereupon immediately after the exposure. 55

Example 37

60 The same charge generation layer and the same charge transport layer as those prepared in Example 36 were successively laminated on an aluminum plate 0.2mm thick. 60

A good toner image was obtained using the photosensitive member thus obtained in the same way as Example 36, except that the corona charging was effected at \oplus 5KV and a negatively chargeable developer was used.

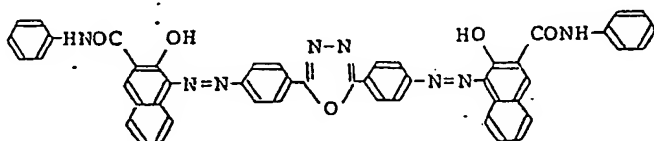
Example 38

A dispersion was prepared by adding 1.0g of β -form copper phthalocyanine to a solution of both 5g of the same hydrazone compound (compound No. H-13) as used in Example 26 and 5g of poly(N-vinylcarbazole) (mol. wt. about 3×10^5) in 150 ml of dichloromethane. The dispersion was coated on the casein layer of the same aluminum plate coated with casein as used in Example 1, and dried to form a photosensitive layer of 11 g/m². The charge bearing characteristics of the photosensitive member thus prepared were measured in the same way as in Example 25, except that the charging was negative. The results were as follows:

$V_0 \ominus 500V$, V_k 88%, E 1/2 28 lux.sec

Example 39

A solution of casein in aqueous ammonia (11.2g of casein, 1g of 28% aqueous ammonia in 222 ml of water) was coated by means of a Meyer bar on an aluminum plate and dried to form a bond layer of 1.0 g/m². Then, 5g of a pigment having the formula



was dispersed in a solution of 2g of vinyl butyral resin (butyral conversion degree 63 mol%) in 95 ml of ethanol by means of a ball mill, and the resulting dispersion was coated on the bond layer by means of a Meyer bar and dried to form a charge generation layer of 0.2 g/m². Then, a solution of both 5g of p-(1-pyrrolidinyl)-benzaldehyde-N',N'-diphenylhydrazone and 5g of polycarbonate of 2,2-bis(4-hydroxyphenyl) propane (mol. wt. about 30,000) in 70 ml of tetrahydrofuran was coated on the charge generation layer and dried to form a charge transport layer of 10 g/m².

The photosensitive member thus prepared was conditioned at 20°C under 65% relative humidity, then charged in the static process by corona charging at $\ominus 5KV$ using the electrostatic copying paper test device mentioned in Example 1, retained in a dark place for 10 seconds, and then exposed to light at 5 lux to examine the charge bearing characteristics. The results were as follows:

$V_0 \ominus 560V$, V_k 91%, E 1/2 7.5 lux.sec

Examples 40-43

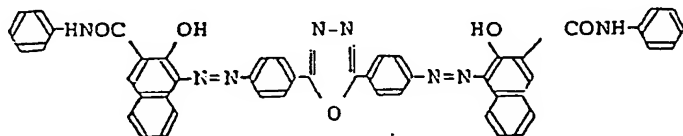
A charge generation layer 0.8 μ thick of selenium-tellurium (tellurium content 10% by weight) was formed by vacuum deposition on an aluminum plate of 100 μ in thickness. Then, a solution of both 5g of a polyester resin (Vylon 200, made by Toyobo Co., Ltd.) and 5g of each hydrazone compound shown in Table 6 in 70 ml of tetrahydrofuran was coated on the charge generation layer and dried to form a charge transport layer of 11 g/m². The charge bearing characteristics of the photosensitive member thus prepared were examined in the same way as Example 39. The results are shown in Table 6.

TABLE 6

Example	Hydrazone compound of formula (1)	Charge bearing characteristics		
		V_0 (-V)	V_k (%)	E 1/2 (lux.sec)
40		580	93	5.8
41		590	91	14.3
42		580	90	10.0
43		550	90	13.2

Example 44

To a solution prepared by dissolving 5g of p-(1-pyrrolidiny)-benzaldehyde-N',N'-diphenylhydrazone and 5g of poly(N-vinylcarbazole) (mol. wt. about 3×10^5) in 70 ml of tetrahydrofuran was added 1.0g of a pigment of the formula



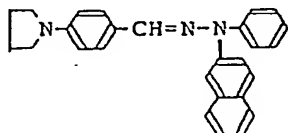
and dispersed by means of ball mill. The dispersion was coated by means of a Meyer bar on the casein layer of the same aluminum plate coated with casein as used in Example 39 and dried to form a 10 g/m^2 coating.

The charge bearing characteristics of the photosensitive member thus prepared were measured in the same way as Example 39, except that the charging was positive. The results were as follows:

$V_o \oplus 520\text{V}$, $V_k 86\%$, $E 1/2 14 \text{ lux.sec}$

Example 45

An aluminum plate of 0.2mm in thickness was fixed in a vacuum device, which was then thoroughly evacuated, and a gas mixture of hydrogen and silane (15 vol% based on hydrogen) was introduced. Then, a charge generation layer of 0.3μ in thickness of amorphous silicon was formed on the substrate by glow discharge applying a 13.5 MHz high-frequency electric field. After atmospheric pressure was brought back in the vacuum device, the sample plate was taken out and a solution of both 5g of a polyester resin (Vylon 200, made by Toyobo Co., Ltd.) and 5g of a hydrazone of the formula



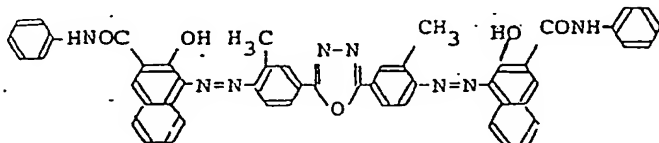
in 150 ml of dichloromethane was coated in the charge generation layer and dried to form a charge transport layer of 10 g/m^2 . The photosensitive member thus obtained was placed in a charging-exposing test device, corona-charged at $\ominus 5\text{KV}$, and subsequently exposed to a pattern of light, which was projected from a tungsten light source through a transmission type test chart. A good toner image was obtained on the surface of the photosensitive member by cascading a positively chargeable developer (containing toner and carrier) thereupon immediately after the exposure.

Example 46

The same charge generation layer and the same charge transport layer as those of Example 45 were successively laminated on an aluminum plate 0.2mm thick. A good toner image was obtained using the photosensitive member thus obtained, in the same way as Example 45, except that the charging was effected at $\oplus 5\text{KV}$ and a negatively chargeable developer was used.

Example 47

A solution of casein in aqueous ammonia (11.2g of casein, 1g of 28% aqueous ammonia in 222 ml of water) was coated by means of a Meyer bar on an aluminum plate to form a bond layer of 1.0 g/m^2 . Then, 5g of a pigment of the formula



was dispersed in a solution of 2g of vinyl butyral resin (butyral conversion degree 63 mol%) in 95 ml of ethanol using a ball mill. The resulting dispersion was coated by means of a Meyer bar on the bond layer and dried to form a charge generation layer of 0.2 g/m^2 . Subsequently, a solution of both 5g of glyoxal-bis(N',N'-diphenylhydrazone) and 5g of polycarbonate of 2,2-bis(4-hydroxyphenyl) propane (mol. wt. about 30,000) in 70 ml of dichloromethane was coated on the charge generation layer and dried to form a charge transport layer of 1.0 g/m^2 .

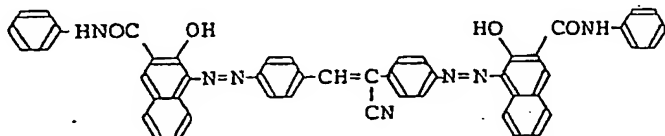
The photosensitive member thus prepared was conditioned at 20°C under 65% relative humidity, then corona-charged at $\ominus 5\text{KV}$ in the static process using the electrostatic copying paper test device mentioned in Example 1, retained in a dark place for 10 seconds, and exposed to light at 5 lux to examine the charge

bearing characteristics. The results were as follows:

$V_o \ominus 600V$, V_k 98%, E 1/2 9.3 lux.sec

5 Example 48

To a solution prepared by dissolving 5g of glyoxal-bis(N',N'-diphenylhydrazone) and 5g of poly(N-vinylcarbazole) (mol. wt. about 3×10^5) in 70 ml of dichloromethane was added 1.0g of a pigment of the formula



15 and dispersed by means of a ball mill. The resulting dispersion was coated by means of a Meyer bar on the casein layer of the same aluminum plate coated with casein as used in Example 47 and dried to form a photosensitive layer of 10 g/m². The charge bearing characteristics of the photosensitive member thus prepared were measured in the same way as Example 47, except that the charging was positive. The results were as follows:

$V_o \oplus 540V$, V_k 90%, E 1/2 16 lux.sec

Examples 49-52

A charge generation layer of selenium-tellurium (tellurium content 10% by weight) of 0.8 μ in thickness was formed by vacuum deposition on an aluminum plate of 100 μ in thickness. A solution of both 5g of a polyester resin (Vylon 200, made by Toyobo Co., Ltd.) and 5g of each hydrazone compound shown in Table 7 in 70 ml of dichloromethane was coated on the charge generation layer and dried to form a charge transport layer of 10 g/m². The charge bearing characteristics of the photosensitive member prepared in this way were measured in the same way as Example 47. The results are given in Table 7.

TABLE 7

Example	Hydrazone compound of formula 1	Charge bearing characteristics		
		V_o (-V)	V_k (%)	E 1/2 (lux.sec)
49		590	93	7.0
50		600	92	25
51		610	90	6.8
52		580	90	10.2

55 Example 53

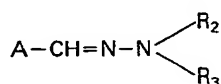
An aluminum base plate of 0.2mm in thickness was fixed in a vacuum device, which was then thoroughly evacuated, and a gas mixture of hydrogen and silane (15 vol% based on hydrogen) was introduced. Then, a charge generation layer 0.3 μ thick of amorphous silicon was formed on the substrate by glow discharge applying a 13.5 MHz high-frequency electric field. After atmospheric pressure was brought back in the vacuum unit, the sample plate was taken out, and a charge transport layer was formed on the charge generation layer in the same way as Example 47. The photosensitive member thus obtained was placed in a charging-exposing test device, corona-charged at $\ominus 5KV$, and subsequently exposed to a pattern of light, which was projected from a tungsten light source through a transmission type test chart. A good toner image was obtained on the surface of the photosensitive member by cascading a positively chargeable developer (containing toner and carrier) thereupon immediately after the exposure.

Example 54

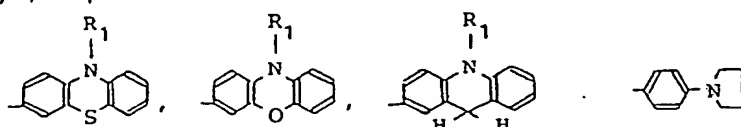
The same charge generation layer and the same charge transport layer as those of Example 53 were successively laminated on an aluminum plate 0.2mm thick. A good toner image was obtained using the photosensitive member thus obtained, in the same way as Example 53, except that the corona charging was effected at $\oplus 5\text{KV}$ and a negatively chargeable developer was used.

CLAIMS

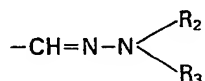
1. An electrophotographic photosensitive member comprising a layer containing a hydrazone compound represented by the formula



- wherein R_2 and R_3 are each unsubstituted alkyl or substituted alkyl, unsubstituted aralkyl or substituted aralkyl, or unsubstituted aryl or substituted aryl, with the proviso that R_2 and R_3 are not simultaneously alkyls, A represents



or



- wherein R_1 is $\text{C}_1\text{-C}_5$ alkyl, unsubstituted aralkyl, or substituted aralkyl.

2. An electrophotographic photosensitive member according to claim 1 wherein said hydrazone compound is selected from N-ethylphenothiazine-3-aldehyde-N',N'-diphenylhydrazone, N-ethylphenoxazine-3-aldehyde-N',N'-diphenylhydrazone, p-(1-pyrrolidinyl)-benzaldehyde-N',N'-diphenylhydrazone, and glyoxal-bis(N',N'-diphenylhydrazone),

3. An electrophotographic photosensitive member according to claim 1 or claim 2, wherein the electrophotographic photosensitive member comprises a conductive layer, a charge generation layer, and a charge transport layer which contains a said hydrazone compound.

4. An electrophotographic photosensitive member according to claim 3, wherein the charge transport layer is over the charge generation layer.

5. An electrophotographic photosensitive member according to claim 4, wherein the electrophotographic photosensitive member comprises on a support in sequence from bottom to top a conductive layer, a bonding layer, a charge generation layer, and a charge transport layer which contains a said hydrazone compound.

6. An electrophotographic photosensitive member according to any of claims 3, 4 or 5, wherein said charge transport layer contains a binder.

7. An electrophotographic photosensitive member according to claim 6, wherein said binder comprises at least one polymer selected from the group consisting of acrylic resins, polystyrene resins, polyester resins, phenoxy resins, polycarbonate resins, silicone resins, epoxy resins, polyurethane resins, and poly(N-vinylcarbazole).

8. An electrophotographic photosensitive member according to any of claims 3 to 7 wherein said charge transport layer has a thickness of $5 - 30\mu$.

9. An electrophotographic photosensitive member according to claim 8, wherein said charge transport layer has a thickness of $8 - 20\mu$.

10. An electrophotographic photosensitive member according to any of claims 3 to 9 wherein said charge generation layer contains a substance selected from selenium, selenium-tellurium, selenium-arsenic, cadmium sulfide, amorphous silicon, pyrylium dyes, thiapyrylium dyes, triarylmethane dyes, thiazine dyes, cyanine dyes, phthalocyanine pigments, perylene pigments, indigo pigments, thioindigo pigments, quinacridone pigments, azo pigments, and polycyclic quinone pigments.

11. An electrophotographic photosensitive member according to any of claims 3 to 9 wherein said charge generation layer contains a disazo pigment.

12. An electrophotographic photosensitive member according to any of claims 3 to 11, wherein said charge generation layer contains a photosensitive organic compound and a binder.

13. An electrophotographic photosensitive member according to claim 12, wherein said binder comprises a polymer selected from a poly(vinyl butyral), poly(vinyl acetate), polyesters, polycarbonates, phenoxy resins, acrylic resins, polyacrylamide, polyamides, polyvinylpyridine resins, cellulosic resins,

urethane resins, epoxy resins, casein, and poly(vinyl alcohol).

14. An electrophotographic photosensitive member according to any of claims 3 to 13, wherein said charge generation layer comprises a vacuum-deposited layer of selenium-tellurium, amorphous silicon, or a perylene dye.

5 15. An electrophotographic photosensitive member according to claim 4, or any of claims 5 to 14 as dependent thereon wherein said bonding layer contains a high-molecular compound selected from casein, poly(vinyl alcohol), water-soluble ethylene-acrylic acid copolymers, and nitrocellulose. 5

16. An electrophotographic photosensitive member according to claim 1, wherein the electrophotographic photosensitive member comprises a photosensitive layer containing a charge generation material and a said hydrazone compound. 10 10

17. An electrophotographic photosensitive member according to claim 16, wherein the charge generation material comprises poly(N-vinyl-carbazole).

18. An electrophotographic photosensitive member according to claim 16 or 17, wherein the charge generation material comprises a disazo pigment.

15 19. An electrophotographic photosensitive member according to claim 16 or 17, wherein the charge generation material comprises a β -form of copper phthalocyanine. 15

20. An electrophotographic photosensitive member according to any of claims 16 to 19 wherein the hydrazone compound is N-ethylphenothiazine-3-aldehyde-N',N'-diphenyl-hydrazone or N-ethylphenoxazine-3-aldehyde-N',N'-diphenyl-hydrazone.

20 21. An electrophotographic photosensitive member substantially as described herein with reference to any one of the Examples. 20

New claims or amendments to claims filed on 16.6.84

Superseded claims all

25 New or amended claims:- 25

CLAIMS

30 1. An electrophotographic photosensitive member comprising a charge generation layer composed of amorphous silicon, and a charge transport layer which contains a hydrazone compound. 30

2. An electrophotographic photosensitive member according to claim 1 wherein the amorphous silicon contains hydrogen atoms.

3. An electrophotographic photosensitive member according to claim 1 or claim 2 wherein the charge transport layer is on the charge generation layer.

35 4. An electrophotographic photosensitive member according to claim 3 wherein the charge transport layer is on a conductive support. 35

5. An electrophotographic photosensitive member for a laser printer comprising a charge generation layer, said charge generation layer comprising a compound selected from the group consisting of selenium, selenium-tellurium, selenium-arsenic, cadmium sulfide, amorphous silicon, pyrylium-dyes or co-crystalline complexes thereof, thiopyrylium dyes or co-crystalline complexes thereof, triarylmethane dyes, thiazine dyes, cyanine dyes, phthalocyanine pigments, perylene pigments, indigo pigments, thioindigo pigments, quinacridone pigments, azo pigments, and polycyclic quinone pigments, and a charge transport layer which contains a hydrazone compound. 40 40

6. An electrophotographic photosensitive member for a laser printer according to claim 5 wherein said charge generation layer comprises a compound selected from amorphous silicon, pyrylium dyes or co-crystalline complexes thereof, thiopyrylium dyes or co-crystalline complexes thereof, phthalocyanine pigments, perylene pigments and azo pigments. 45 45

7. An electrophotographic photosensitive member for a laser printer according to claim 5 wherein said charge generation layer contains a compound selected from pyrylium dyes or co-crystalline complexes thereof, thiopyrylium dyes or co-crystalline complexes thereof, phthalocyanine pigments and azo pigments, and a binder. 50 50

8. An electrophotographic photosensitive member for a laser printer according to any of claims 5 to 7 wherein said charge generation layer contains a disazo pigment.

9. An electrophotographic photosensitive member for a laser printer according to any of claims 5 to 7 wherein said charge generation layer contains a copper phthalocyanine compound. 55 55